The Electronic Absorption Spectra of 2-Substituted-4-*NN*-diethylamino-4'-nitroazobenzene Dyes and Their Monoacid Cations: The Applicability of Dewar's Rules to These and Related Dyestuffs

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A number of 2-substituted-4-*NN*-diethylamino-4'-nitroazobenzene dyestuffs have been prepared and their visible electronic spectra determined in neutral and acidic media. In ethanol, electron-donating substituents caused a bathochromic shift of $\lambda_{max.}$, the extent of which was proportional to their electron-donating ability. Electron-withdrawing substituents caused a correspondingly smaller hypsochromic shift. When the 2-substituent was either carboxy, hydroxy, or acylamino, the results could be explained in terms of hydrogen-bonding to the azo-link. The tinctorial strength of the dyes, as expressed by the area under the absorption curve, remained essentially constant over a 100 nm range.

In ethanolic hydrogen chloride, electron-donating substituents stabilised the azonium tautomer and generally produced a hypsochromic shift of $\lambda_{max.}$; electron-withdrawing substituents generally had the opposite effect. With the more powerful electron-donating groups, the rare phenomenon of negative halochromism was observed. The general applicability of Dewar's Rules to both neutral and protonated 4-aminoazobenzene dyes is questioned.

AZO-DYES are very important commercially: within this class, those derived from 4-aminoazobenzene are valuable dyes for polyester fibres. Despite this, surprisingly little systematic work has been done regarding their colour and constitution. Previous work on 4-aminoazobenzene dyes [1-12] and their monoacid cations [6-16] has dealt mainly with substituent effects in the diazo-component-ring D of formula (1). The effect of substituents in the coupling

unstarred carbon atom, should cause a large hypsochromic shift of $\lambda_{max.}$. Conversely, any electron-donating substituent at a starred carbon atom, or electron-withdrawing substituent at an unstarred carbon atom, should cause a smaller bathochromic shift.

Castelino and Hallas [6] used these rules to explain the bathochromic shift of azo-dyes (2) derived from julolidine relative to their *NN*-diethylaniline counterparts, the

(1)

(2)

(3)

(4)

(5)

(6)
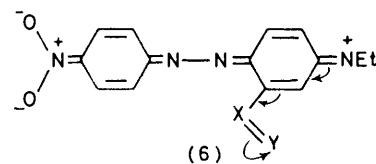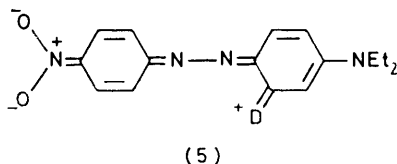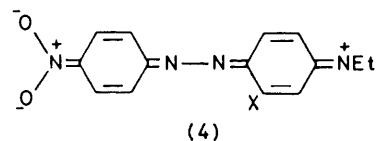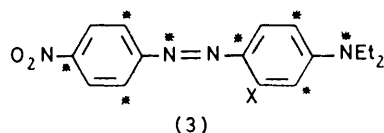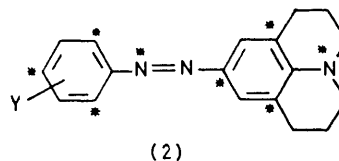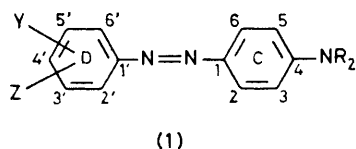
component (ring c) has been neglected. In the few examples reported,[5,6] electron-donating substituents in the 3- and 5-positions produced, in the absence of steric effects, a bathochromic shift of $\lambda_{max.}$; electron-withdrawing groups produced a hypsochromic shift.[7] These observations are in agreement with the predictions of Dewar's Rules,[17] derived from Perturbational Molecular Orbital (PMO) theory, which predict that any electron-withdrawing substituent at a starred carbon atom, or any electron-donating substituent at an

electron-donating alkyl groups being attached to the starred 3- and 5-positions. For the unstarred carbon atoms 2 and 6 in formula (1), Dewar's Rules predict a relatively large hypsochromic shift for electron-donating groups and a smaller bathochromic shift for electron-withdrawing groups. The reported [2,8] bathochromic effect of a methyl group in the 2-position is at variance with these predictions. To ascertain if substituents in general disobey Dewar's Rules in the 2-position, a series of dyes of formula (3) has been prepared, where X is a

variety of electron-donating and electron-withdrawing groups.

para-Nitroaniline was selected as the diazo-component for two reasons. First, the unique electron acceptor properties of a 4-nitro-group [2] expands the available shade gamut thus facilitating the investigation of spectral shifts due to the X-substituent. Secondly, diazo-*p*-nitroaniline is one of the more electrophilic diazo-components which couples readily, even with deactivated amines, thus minimising synthetic problems. *NN*-Diethylaniline derivatives were selected as coupling components to facilitate comparison with the bulk of published work on 4-aminoazobenzene dyes.

RESULTS AND DISCUSSION

Spectra in 95% Ethanol.—All the dyes of formula (3) showed a characteristic single, reasonably symmetrical absorption band in the visible region of the spectrum. Their $\lambda_{max.}$ and $\varepsilon_{max.}$ values are recorded in Table 1.

TABLE 1

Visible absorption spectral data for dyes (3) in 95% ethanol (λ in nm, ε in 1 mol^{-1} cm^{-1}, and ν in cm^{-1})

X	$\lambda_{max.}$	$\Delta\lambda$	$10^{-3}\varepsilon_{max.}$	$\Delta\nu_{\frac{1}{2}}$	$10^{-8}(\varepsilon_{max.} \times \Delta\nu_{\frac{1}{2}})$
CF$_3$	467	-19	32.4	5 400	1.75
F	469	-17	28.8	6 100	1.76
NO$_2$	470	-16	31.8	5 000	1.59
CN	472	-14	32.4	4 600	1.49
SO$_2$NMe$_2$	471	-15	31.4	5 100	1.60
Cl	472	-14	33.8	5 000	1.69
Br	472	-14	33.6	5 000	1.68
OH	473	-13	49.0	4 100	2.06
I	476	-10	32.8	4 900	1.61
O:P(OEt)$_2$	476	-10	31.1	4 700	1.46
SO$_2$Me	477	-9	32.4	4 700	1.52
CO$_2$Et	479	-7	32.2	5 000	1.61
EtNAc	482	-4	36.0	4 900	1.76
SO$_2$NH$_2$	484	-2	31.6	4 800	1.52
H	486	0	34.0	5 000	1.70
Ac	488	$+2$	36.0	4 800	1.73
CO$_2$H	493	$+7$	30.0	5 300	1.59
Me	497	$+11$	33.2	4 900	1.63
NHSO$_2$Me	498	$+12$	43.5	4 100	1.78
OMe	501	$+15$	32.8	5 000	1.64
NHAc	511	$+25$	47.0	3 900	1.99
SMe	513	$+27$	35.5	4 800	1.70
NH$_2$	514	$+28$	45.0	4 200	1.89
NHCONH$_2$	518	$+32$	41.0	4 300	1.76
NEt$_2$	542	$+56$	31.0	6 100	1.89
O$^-$	567	$+81$	43.0	3 700	1.59

The general trend is that electron-donating substituents produce a bathochromic shift of $\lambda_{max.}$ and electron-withdrawing substituents a smaller hypsochromic shift. Certain substituents markedly affect $\lambda_{max.}$. Thus, by a suitable choice of X in formula (3), the shade can be varied from orange ($\lambda_{max.}$ 467 nm) to violet ($\lambda_{max.}$ 567 nm), a difference of 100 nm.

Valence Bond/resonance theory, propounded by Pauling [18] and Bury,[19] and later applied to aminoazobenzene dyes by Sawicki [1] and Bridgeman and Peters,[2] successfully explains the experimental results. In this treatment, the uncharged structure (3) is considered to make the major contribution to the ground state,

whereas the charge-separated form (4) makes a significant contribution to the excited state.

Any factors which reduce the energy difference between these two states cause a bathochromic shift of $\lambda_{max.}$; conversely, factors which increase the energy difference cause a hypsochromic shift. For dyes of formula (3), electron-donating X groups (D) stabilise the excited state by a contribution from canonical forms such as (5), in which the donor group shares the positive charge by delocalisation of its lone pair of electrons into the π-electron system. In the case of a methyl group, stabilisation is effected by hyperconjugation reinforced by a $+I$ inductive effect. The magnitudes of the shifts are directly comparable to the electron-donating power of the substituent, increasing in the order H < Me < OMe < NHCOR $\sim$ SMe $\sim$ NH$_2$ $\ll$ NEt$_2$ < O$^-$ in 95% ethanol (Table 1) for the more common electron-donating substituents. The observation that amino- and acylated amino-groups produce similar bathochromic shifts of $\lambda_{max.}$ suggest that effects additional to electronic ones, such as hydrogen-bonding, may be operative in these cases. However, electronic factors are clearly responsible in the case of the substituents producing the largest bathochromic shifts, namely NEt$_2$ and O$^-$, a difference of 81 nm being observed between (3; X = H and O$^-$).

Electron-withdrawing substituents (–X=Y) can destabilise structure (4) by both mesomeric [*e.g.* (6)] and inductive effects, by tending to reduce the electron density at an already electron-deficient atom. The smaller magnitude of the observed hypsochromic shift [only 19 nm separate (3) X = H and CF$_3$)], plus the fact that fluorine and trifluoromethyl groups produce similar shifts to cyano- and nitro-groups, strongly suggest that the effect is primarily an inductive one. Furthermore, this postulate does not contradict one of the conditions of resonance theory, namely, that the actual resonance hybrid is more stable than any of the individual canonical forms.

The fact that the ' rod-like ' cyano-group produces a definite hypsochromic shift of $\lambda_{max.}$ is important, since steric factors will be at a minimum [3,4] and the effect can be ascribed solely to electronic factors. For some of the larger groups, steric interaction with the azo-nitrogen lone-pair orbitals could be responsible for part of the hypsochromic shift. It is known,[3] for example, that a nitro-group *ortho* to an azo-linkage in the diazo-component [ring D of (1)] produces a considerably smaller bathochromic shift than when it is in the *para*-position.

The dyes (3) exhibit positive solvatochromism (Table 2), typical of compounds in which the excited state is more polar than the ground state. Also, dipole-moment determinations on a series of 4-*NN*-dimethylaminoazobenzene dyes,[20] show that the contribution of charge-separated structures such as (4) to the ground state of the molecule is no more than 7%. These two observations, although not supplying conclusive evidence in favour of the above Valence Bond/resonance explanation, are certainly consistent with it.

X	Dioxan	95% Ethanol	Formamide
NO_2	459 (29.6)	470 (31.8)	498 (29.2)
H	476 (34.4)	486 (34.0)	512 (32.4)
Me	486 (33.8)	497 (33.2)	526 (32.6)

Dielectric constants: dioxan 2.2, ethanol 24.3, formamide 109 at 20 °C.

Tinctorial Strength of the Neutral Dyes in 95% *Ethanol.* —This neglected parameter is of vital importance in industrial dyestuffs chemistry, since it is one of the main factors influencing the economics of a dye. For reasonably symmetrical absorption curves, a good approximation to tinctorial strength, as expressed by the area

strated that on protonation a tautomeric equilibrium exists between the azonium form (8) and the ammonium form (9). The resonance-stabilised azonium form (8A) ◄─► (8B) is generally intensely coloured and absorbs at longer wavelength than the unprotonated dye (7), whereas the colourless ammonium form absorbs at shorter wavelengths than (7). The ammonium tautomer resembles azobenzene, absorbing in the u.v. region at *ca.* 320 nm.

Data from the absorption spectra of the dyes of formula (3), measured in ethanol–concentrated hydrochloric acid (2 : 1), are recorded in Table 3.

Electron-donating X groups stabilise the azonium tautomer (8; Y = 4-NO_2, R = Et) and displace the equilibrium in favour of this tautomer. When X is an

(7)

(8A)

(8B)

(9)

H_3O^+
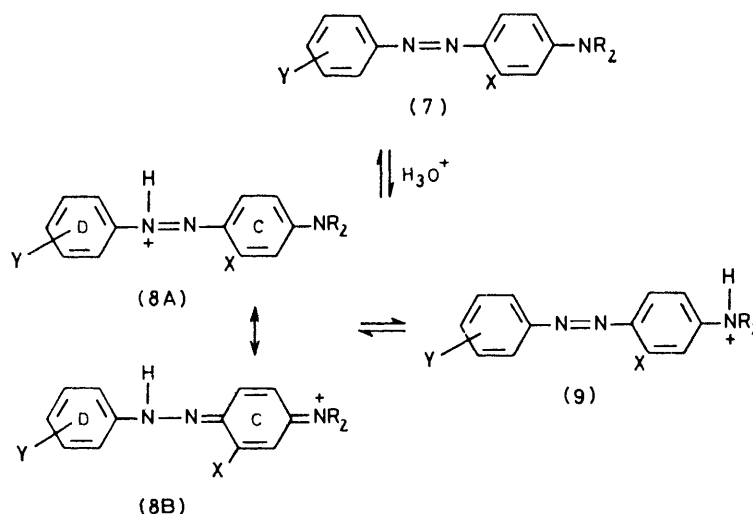
under the curve, is given by the product of $\varepsilon_{max.}$ and half-band width, $\Delta\nu_{\frac{1}{2}}$ (in cm^{-1}). Table 1 shows that the tinctorial strength of the dyes (3), measured in this way, remain fairly constant over a range of 100 nm (or 3 800 cm^{-1}). The only minor increases are associated with dyes having hydroxy- or acylamino-substituents, where hydrogen-bonding effects occur (see later).

In MO theory, the oscillator strength, f, the theoretically calculable parameter directly related to the area under the curve, is inversely proportional to the wavelength of absorption [21] [equation (1)], where ν_m is the

$$f = 4.703 \times 10^{29} \times M^2 \times \nu_m \qquad (1)$$

mean absorption frequency of the band, expressed in cm^{-1}, *i.e.* $\nu_m = 1/\lambda_{max.}$. In other words, provided the transition dipole moment, M, remains constant, tinctorial strength should decrease as the wavelength of maximum absorption ($\lambda_{max.}$) increases. The essentially constant tinctorial strength of the dyes (3) means that the transition dipole moment must increase sufficiently with increasing wavelength to just compensate this decrease.

Spectra in Ethanol–10M-*Hydrochloric Acid* (2 : 1).— Several workers [8,10,12–15] have studied the effect of acid on aminoazobenzene dyes (7; X = H) and demon-

electron-withdrawing group, the equilibrium is displaced more in favour of the ammonium tautomer (9; Y = 4-NO_2, R = Et). The effect of electron-donating and electron-withdrawing groups on the colour of the azonium tautomer is opposite to their effect on the neutral dyes. Thus, electron-donating groups generally produce a hypsochromic effect whereas electron-withdrawing groups generally produce a bathochromic effect. When X is a powerful electron-donating group such as amino, diethylamino, acylamino, thiomethoxy, and methoxy, the rare phenomenon of negative halochromism [9,22] is observed, whereby the azonium form absorbs at shorter wavelengths than the neutral dye.

The absorption curves of the azonium tautomers are narrower than those of the corresponding neutral dyes in ethanol, as shown by their half-band widths [$\Delta\nu_{\frac{1}{2}}$ in wavenumbers (cm^{-1})]. These are in the region of 3 300 cm^{-1} compared with *ca.* 5 000 cm^{-1} for the neutral dyes. As a consequence, the colours of the azonium tautomers are brighter than those of the neutral dyes.

The dyes containing powerful, electron-donating groups such as amino, hydroxy, methoxy, acylamino, and diethylamino, are readily protonated in acetic acid to form predominantly the azonium tautomer, indicating

Table 3

Spectral data for the azonium (8) and ammonium (9) tautomers in EtOH–10M-HCl (2 : 1, v/v) (λ in nm, ε in 1 mol^{-1} cm^{-1}, and ν in cm^{-1})

X	Azonium tautomer				Ammonium tautomer	
	$\lambda_{max.}$	$\Delta\lambda$	$10^{-3}\varepsilon_{max.}$	$\Delta\nu_{\frac{1}{2}}$	$\lambda_{max.}$	$10^{-3}\varepsilon_{max.}$
NH_2	482	-33	63.8	3 500		
OMe	486	-29	70.0	3 400		
OH	489	-26	61.0	3 500		
NHAc	493	-22	32.1	4 500		
$NHCONH_2$	500	-15	47.3	3 700		
$NHSO_2Me$	504	-11	61.2	3 300		
F	505	-10	50.0	3 300	ca. 323	6.5
SMe	508	-7	63.0	3 500		
Me	513	-2	63.0	3 200	ca. 357	15.5
					ca. 320	18.0
NO_2	514	-1	18.0	3 400	ca. 360	26.0
					ca. 318	28.0
H	515	0	43.5	3 100	ca. 326	16.0
Cl	515	0	57.5	3 100	ca. 326	11.5
I	518	$+3$	45.6	3 200	323	13.8
Br	520	$+5$	52.2	3 300	ca. 325	15.6
EtNAc	520	$+5$	5.0	3 300	313	12.25
$HNEt_2^+$	520	$+5$	37.5	3 900	ca. 327	16.8
CO_2H	ca. 525	$+10$	14.0	3 400	320	18.5
CO_2Et	ca. 525	$+10$	15.5	3 600	ca. 320	23.0
CF_3	ca. 530	$+15$	21.0	3 200	ca. 324	22.8
$O{:}P(OEt)_2$	ca. 532	$+17$	23.7	3 200	ca. 325	18.6
SO_2NMe_2	533	$+18$	18.0	3 300	318	27.8
SO_2NH_2	ca. 534	$+19$	26.0	3 200	325	19.0
SO_2Me	ca. 535	$+20$	22.8	3 300	ca. 324	23.7
Ac	548	$+33$	56.3	3 200		
* CN	ca. 550	$+35$	9.0	3 200	ca. 320	13.5

* Unstable—the $\varepsilon_{max.}$ values of both tautomers decrease by about 70% after 5 min at 20 °C.

the relative stability of these compounds. The dye (7; Y = 4-NO_2, R = Et, X = NEt_2) exhibits different $\lambda_{max.}$ values in (2 : 1) ethanolic hydrogen chloride ($\lambda_{max.}$ 520 nm) and glacial acetic acid ($\lambda_{max.}$ 480 nm). In acetic acid, the predominant species is the monoacid azonium

containing carboxy-groups in the *ortho* position of the diazo component, *i.e.* (8; Y = 2'-CO_2H, X = H) has been reported.[12a, 23]
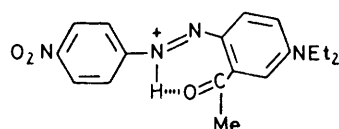
Hydrogen-bond formation with the oxygen atom of the methoxy-group is believed to be responsible for the
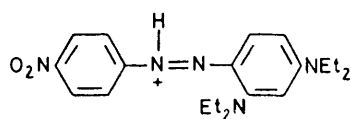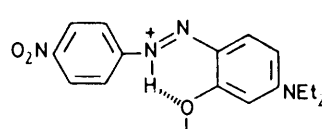

(10)
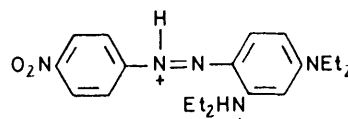
(11)

(12)

(13)

tautomer (10). The unprotonated diethylamino-group functions as an electron-donating species, producing the expected hypsochromic shift. In ethanolic hydrogen chloride, the diacid species (11) predominates. Here, the protonated amino-group functions in an electron-withdrawing capacity, causing a bathochromic shift.

A surprising observation is the protonation of (7; Y = 4-NO_2, R = Et, X = Ac) in acetic acid. In contrast to the general trend, the electron-withdrawing acetyl group stabilises the azonium form, which is a bright violet ($\lambda_{max.}$ 548 nm, $\varepsilon_{max.}$ 56 300) (Tables 3 and 4). Its stability is probably associated with hydrogen-bond formation involving the carbonyl oxygen atom (12).* However, a similar stabilisation of azonium tautomers

exceptional stability of the azonium tautomer (8; Y = 4-NO_2, R = Et, X = OMe). In this case, a stable six-membered chelate system is formed (13). Ross and Warwick observed a similar effect in related aminoazobenzene dyes.[23]

Effect of Carboxy-, Hydroxy-, and Acylamino-groups in the Neutral Dyes.—(i) *The carboxy-dye* (14). The spectral data in various solvents and the effect of added base are recorded in Table 5.

In every solvent except 95% ethanol, the carboxy-

* It is curious that the carboxy and ethoxycarbonyl dyes (Table 3) are capable of hydrogen-bonding similar to that of the acetyl dye, but only the latter shows exceptional stabilisation of the azonium tautomer.
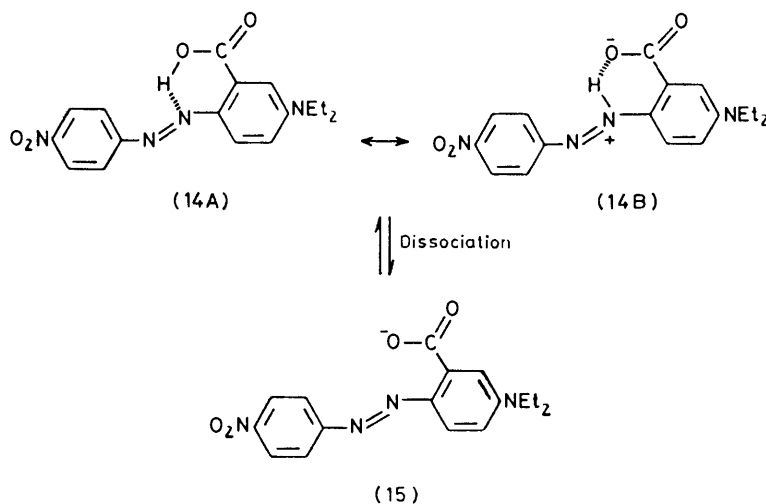
X	$\lambda_{max.}$	$\Delta\lambda$	$10^{-3}\varepsilon_{max.}$	$\Delta\nu_{\frac{1}{2}}$
CF$_3$	466	-23	33.2	4 700
F	472	-17	24.6	6 100
NO$_2$	467	-22	30.4	5 000
CN *	471	-18	22.8	4 700
SO$_2$NMe$_2$	470	-19	30.4	4 900
Cl	472	-17	33.0	4 900
Br	474	-15	33.2	5 000
OH	471	-18	55.0	3 700
I	477	-12	31.8	4 900
O:P(OEt)$_2$	475	-14	31.6	4 700
SO$_2$Me	478	-11	34.2	4 700
CO$_2$Et	479	-10	31.2	5 000
EtNAc	475	-14	34.0	5 100
SO$_2$NH$_2$	484	-5	33.0	4 800
H	489	0	33.4	4 900
COMe	546	$+57$	46.0	3 700
CO$_2$H	523	$+34$	32.8	4 100
Me	507	$+18$	33.2	3 600
NHSO$_2$Me	495	$+6$	42.5	4 000
OMe	480	-9	62.5	3 400
NHAc	511	$+22$	48.0	3 900
SMe	512	$+23$	44.5	4 000
NH$_2$	476	-13	56.5	3 500
NHCONH$_2$	502	$+13$	48.0	3 700
NEt$_2$	480	-9	43.0	3 800

* The $\varepsilon_{max.}$ figure is too low since the dye is unstable in acetic
acid: after 1 h, the $\varepsilon_{max.}$ dropped to 4 000 (the initial measure-
ment was taken after ca. 5 min).

dye exhibits an appreciable bathochromic shift of $\lambda_{max.}$
relative to (3; X = H). Addition of base causes a
hypsochromic shift, but base has no effect on its spectrum
in 95% ethanol. Therefore, in the latter solvent, the
carboxy-dye must already be dissociated. Addition-
ally, because of the slight bathochromic shift of (15)

It is postulated that the undissociated carboxy-dye-
stuff exists as a resonance hybrid of (14A) and (14B).
The dipolar form (14B) resembles the azonium tautomer
(8; Y = 4-NO$_2$, R = Et, X = CO$_2$H), except the proton
is attached to the α-azo-nitrogen atom. Hence, the
observed bathochromic shift of the undissociated
carboxy-dye arises from the contribution of (14B), by
analogy with the bathochromic effect of an electron-
withdrawing group X on the azonium tautomer (8;
Y = 4-NO$_2$, R = Et) (Table 3).

(ii) *The hydroxy-dye.* This exhibits an anomalous
hypsochromic shift of $\lambda_{max.}$ in 95% ethanol: the analo-
gous methoxy-dye shows the expected bathochromic
shift (Table 1). Since hydroxy- and methoxy-groups
have comparable electron-donating abilities, effects
additional to electronic ones are indicated.

Hydroxy-groups *ortho* to an azo-linkage are known to
undergo intramolecular hydrogen-bonding onto the
β-nitrogen atom of the azo-group,[24] to form a stable six-
membered chelate ring system. I.r. data on (3; X =
OH) confirm that the dye exists in an intramolecularly
hydrogen-bonded form both in the solid state and in
carbon tetrachloride solution.

The spectral data in Table 6 show that in every solvent,
the hydroxy-dye has a substantially higher $\varepsilon_{max.}$ and
narrower $\Delta\nu_{\frac{1}{2}}$ relative to (3; X = H). Furthermore, the
$\lambda_{max.}$ values of (3; X = OH) are relatively insensitive
to solvent polarity, since there is only a 2 nm difference
between a solution of the dye in cyclohexane (dielectric
constant 2) and formamide (dielectric constant 109).
This contrasts with the pronounced positive solvato-

(14A)   (14B)

Dissociation

(15)

relative to (3; X = H), the ionised carboxy-group
functions as a weak electron-donating substituent.

It is known [23] that a carboxy-group *ortho* to an azo-
linkage forms an intramolecular hydrogen-bond with the
α-nitrogen atom of the azo-group, a stable six-membered
chelate ring being formed. I.r. spectra on (3; X =
CO$_2$H) confirm that this dye also exists in an intra-
molecularly hydrogen-bonded form, both in the solid
state and in carbon tetrachloride solution.

chromism of (3; X = H), where 57 nm separate the
$\lambda_{max.}$ values in the same two solvents. It has been
postulated [25] that the large bathochromic shifts of ca.
50 nm on addition of water to ethanolic solutions of
azo-dyes is caused by intermolecular hydrogen-bonding
between the water molecules and the azo-group. The
solvent insensitivity of the hydroxy-dye arises because
of the strong intramolecular hydrogen-bond, which
effectively limits solvation at the azo-group. In polar

TABLE 5

The effect of base on the spectra of (3; X = CO_2H and H) in various solvents (λ in nm, ν in cm⁻¹, ε in 1 mol⁻¹ cm⁻¹)

	X	Cyclohexane [a]	Cyclohexane + BuᵗO⁻	Dioxan	Dioxan [a,b] + BuᵗO⁻	95% Ethanol	95% Ethanol [a,b] + BuᵗO⁻	Glacial acetic acid
$\lambda_{max.}$	CO_2H	497 525	460	500	482	493	492	523
$10^{-3}\varepsilon_{max.}$		30.8	22.0	29.6	32.8	30.0	30.0	32.8
$\Delta\nu_{\frac{1}{2}}$		3 500	4 800	5 000	5 500	5 300	5 300	4 100
$\lambda_{max.}$	H	455 480sh	c	476	c	486	c	489
$10^{-3}\varepsilon_{max.}$		37.0		34.4		34.0		33.4
$\Delta\nu_{\frac{1}{2}}$		4 400		4 600		5 000		4 900
$\Delta\lambda$		+42	+5	+24	+6	+7	+6	+34

[a] In t-butyl alcohol. [b] Similar effects were observed when aqueous solutions of Et₄NOH and NaOH were used. [c] No change on addition of base.

TABLE 6

The effect of base on the spectra of (3; X = OH and H) in various solvents (λ in nm, ε in 1 mol⁻¹ cm⁻¹, and ν in cm⁻¹)

|	X	Cyclohexane	Cyclohexane + base [a]	95% Ethanol	95% Ethanol + base [a]	Formamide	Formamide + base [a]	Glacial acetic acid
$\lambda_{max.}$	OH	478 (main peak) 499	548	473	567	480	589	471
$10^{-3}\varepsilon_{max.}$		51.5	35.0	49.0	43.0	49.5	41.0	55.0
$\Delta\nu_{\frac{1}{2}}$		3 400	3 800	4 100	3 700	3 800	3 400	3 700
$\lambda_{max.}$	H	455 480sh	b	486	b	512	b	489
$10^{-3}\varepsilon_{max.}$		37.0		34.0		32.4		33.4
$\Delta\nu_{\frac{1}{2}}$		4 400		5 000		4 900		4 900
$\Delta\lambda$		+23	+93	-13	+81	-32	+77	-18

[a] Potassium t-butoxide in t-butyl alcohol. sh = Shoulder. [b] No change on addition of base.

solvents, the positive solvatochromism of (3; X = H) results in this dye being more bathochromic than (3; X = OH); in cyclohexane, the reverse is true.

It is suggested that the hydroxy-dye is a resonance hybrid to which canonical forms (16A), (16B), and (16C) make the major contributions. Since the dipolar form (16B) resembles an azonium tautomer containing a

probably in equilibrium with the azonium tautomer (17), since the $\varepsilon_{max.}$ of the hydroxy-dye approaches that of (17) (Tables 3 and 6).

In contrast to the carboxy-dye, dissociation of the hydroxy-group only occurs on the addition of strong base. As expected, the resultant ionised dye (18) is markedly bathochromic relative to (3; X = H).

(16A)   (16B)   (16C)

(18)   (17)
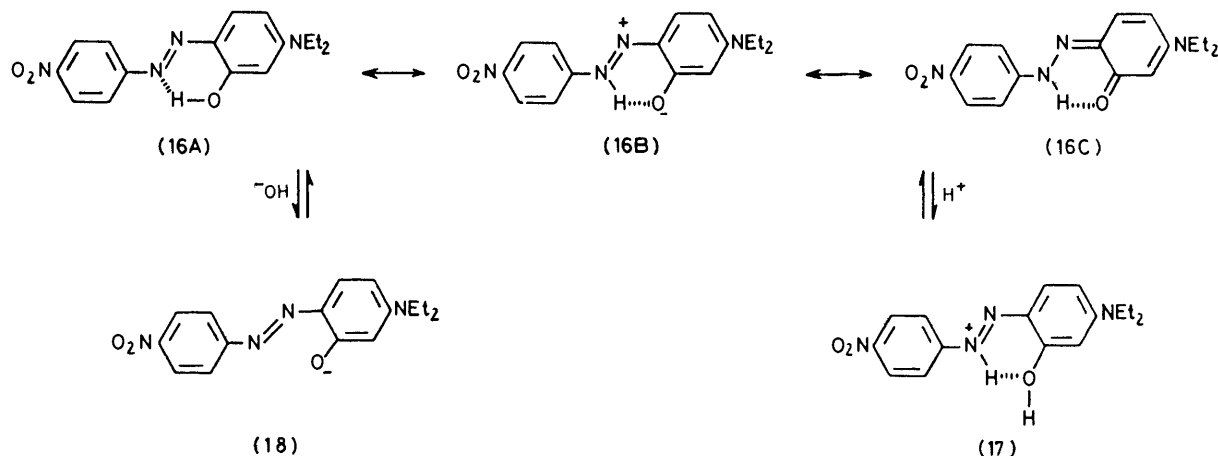
powerful electron-donating substituent, it should exhibit similar spectroscopic properties to such azonium compounds. The observed $\varepsilon_{max.}$ and $\Delta\nu_{\frac{1}{2}}$ values, which are intermediate between those for the neutral dyes and the azonium tautomers (Tables 3 and 6), are in agreement with this explanation. The superior electron-donating ability of an ionised hydroxy-group relative to hydroxy also accounts for the larger hypsochromic shift of the neutral dye (16) in 95% ethanol, relative to the corresponding azonium tautomer (17). In glacial acetic acid, the intramolecularly hydrogen-bonded compound (16) is

(iii) The amino- and acylamino-dyes. I.r. spectra on the dyes (3; X = NHAcyl) show that they are intramolecularly hydrogen-bonded in carbon tetrachloride solution, as shown in (19A). This is in agreement with Sawicki and Gerber's observation of such bonding in 2-aminoazobenzene.[26] The situation is, therefore, similar to that for the hydroxy-dye, except the intramolecular hydrogen-bond is weaker. Thus, the dyes show an increase in $\varepsilon_{max.}$ and a narrower $\Delta\nu_{\frac{1}{2}}$ relative to (3; X = H), both effects arising from the contribution of the dipolar form (19B), which resembles the azonium

TABLE 7

Spectra of the neutral dyes (3; X = H, NHAcyl and NH_2) in various solvents (λ in nm, ε in 1 mol^{-1} cm^{-1}, and ν in cm^{-1})

X	Cyclohexane			Dioxan			Acetic acid			95% Ethanol			Formamide		
	$\lambda_{max.}$	$\varepsilon_{max.}$ 10^{-3}	$\Delta\nu_{\frac{1}{2}}$	$\lambda_{max.}$	$\varepsilon_{max.}$ 10^{-3}	$\Delta\nu_{\frac{1}{2}}$	$\lambda_{max.}$	$\varepsilon_{max.}$ 10^{-3}	$\Delta\nu_{\frac{1}{2}}$	$\lambda_{max.}$	$\varepsilon_{max.}$ 10^{-3}	$\Delta\nu_{\frac{1}{2}}$	$\lambda_{max.}$	$\varepsilon_{max.}$ 10^{-3}	$\Delta\nu_{\frac{1}{2}}$
H	455, 480sh	37.0	4 400	476	34.4	4 600	489	33.4	4 900	486	34.0	5 000	512	32.4	4 900
$NHSO_2Me$	480	*	4 000	495	42.0	4 000	495	42.5	4 000	498	43.5	4 100	507	33.0	4 700
NHAc	498	*	3 500	513	49.0	3 600	511	48.0	3 900	511	47.0	3 900	526	36.5	4 100
$NHCONH_2$	498	*	3 600	518	42.0	3 600	502	48.0	3 700	518	41.0	4 300	534	32.0	4 400
NH_2	476, 496	41.0	4 100	502	38.0	4 300	476	56.5	3 500	514	45.0	4 200	530	33.5	4 400

* Accurate values could not be obtained because of low solubility. sh = Shoulder

tautomer (20), to the resonance hybrid. However, the weaker intramolecular hydrogen-bond is responsible both for their behaviour in formamide, and for their bathochromic shift of $\lambda_{max.}$ relative to (3; X = H) (Table 7).

the arylazo-residue and the ethylacetylamino-substituent (22).

In this non-planar conformation, steric effects are minimal, but the overlap of the nitrogen lone-pair of electrons is diminished to the extent that there is no

(19A)   (19B)

strong base   acid

(21)   (20)
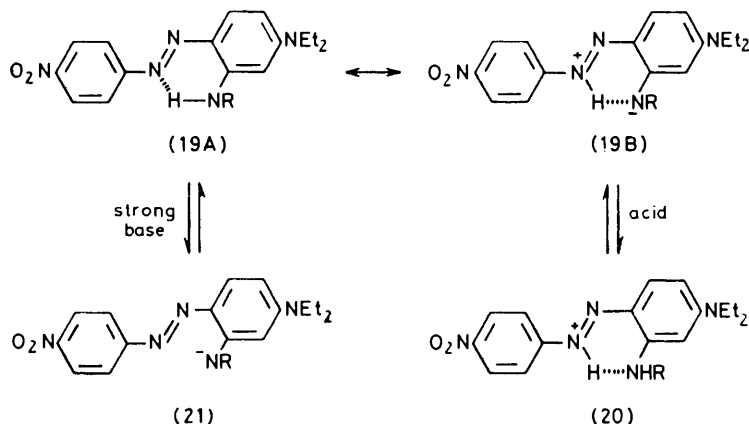
Because of the polarity of formamide and its chemical similarity to an acylamino-group, inter- rather than intra-molecular hydrogen-bonding predominates; hence, the $\varepsilon_{max.}$ and $\Delta\nu_{\frac{1}{2}}$ values of (3; X = NHAcyl and NH_2) become similar to those of (3; X = H) (Table 7). The dyes (3; X = NHAcyl and NH_2) exhibit a positive solvatochromic effect, greater than that of the hydroxy-dye, but less than for (3; X = H). Thus, the difference in $\lambda_{max.}$ of ca. 30 nm for the dyes in cyclohexane and formamide, compares to a 2 nm difference for the hydroxy-dye (Table 6) and a 57 nm difference for (3; X = H) (Tables 6 and 7). As a result, the former dyes are not only more bathochromic than the latter in cyclohexane, as was also the case for the hydroxy-dye, but in every solvent, although the difference decreases with increasing solvent polarity. Indeed, for the dye (3; X = $NHSO_2Me$) in formamide, the changeover point has been reached, since it is now hypsochromic relative to (3; X = H) (Table 7).

In the N-ethylated acetylamino-dye (3; X = EtNAc), intramolecular hydrogen-bonding is absent. As a result, the dye exhibits a hypsochromic shift of $\lambda_{max.}$, a decrease in $\varepsilon_{max.}$, and an increase in $\Delta\nu_{\frac{1}{2}}$, relative to (3; X = NHAc) (Table 1). Furthermore, molecular models indicate that the increased steric hindrance due to the bulky ethylacetylamino-group causes twisting about the aryl–nitrogen bond, with consequent non-coplanarity of

mesomeric effect from the ethylacetylamino-group: only the inductive effect of the electronegative nitrogen atom now operates. Therefore, the dye should have a similar $\varepsilon_{max.}$ to the parent compound (3; X = H), and absorb at slightly shorter wavelengths; this is observed.

lone pair orbital
(22)
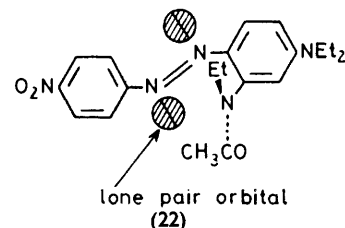
Though the hydrogen atom of an acylamino-group is generally less acidic than that of a hydroxy-group, it can be abstracted with a strong base such as potassium t-butoxide: the spectral data of the neutral (19) and ionised (21) dyes are recorded in Table 8.

The significant features are the decrease in $\varepsilon_{max.}$, increase in $\Delta\nu_{\frac{1}{2}}$, and bathochromic shift of $\lambda_{max.}$ on addition of potassium t-butoxide. The lower $\varepsilon_{max.}$ values of the ionised dyes are compensated by the increase in $\Delta\nu_{\frac{1}{2}}$, so that their tinctorial strength is about equal to that of the neutral dyes. This behaviour is reminiscent of the hydroxy-dye, apart from the increase in $\Delta\nu_{\frac{1}{2}}$ on ionisation. However, the latter effect is not unexpected since the only analogous dye containing a powerful

TABLE 8

Spectra of the neutral dyes (3; X = NHAcyl and NH_2) in Bu^tOH,[a] and Bu^tOH plus 100 mol/mol of Bu^tOK[b] (λ in nm, ε in $l\ mol^{-1}\ cm^{-1}$, and ν in cm^{-1})

X	$\lambda_{max.}$	$\Delta\lambda$	$10^{-3}\varepsilon_{max.}$	$\Delta\nu_{\frac{1}{2}}$	$10^{-8}(\varepsilon_{max.} \times \Delta\nu_{\frac{1}{2}})$	Solvent
$NHSO_2Me$	490	36	40.5	4 000	1.62	a
*NSO_2Me^-	526		31.0	5 100	1.58	b
$NHCOMe$	504	13	45.5	3 900	1.77	a
NAc^-	517		31.5	5 100	1.61	b
$NHCONH_2$	512	14	37.5	4 100	1.54	a
$NCONH_2^-$	526		30.5	5 100	1.56	b
NH_2	508	0	42.0	4 300	1.81	a
NH_2	508		42.0	4 300	1.81	b

* Similar effects were observed with Et_4NOH and NaOH.

nitrogenous electron-donating substituent, (3; X = NEt_2), also has a broad absorption curve ($\Delta\nu_{\frac{1}{2}} = 6\ 100$ cm^{-1}, Table 1).
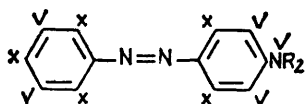

FIGURE 1 Applicability of Dewar's rules to neutral 4-amino-azobenzene dyes: $\sqrt{}$ signifies correct prediction of substituent effects by Dewar's rules; $\times$ signifies incorrect prediction of substituent effects by Dewar's rules
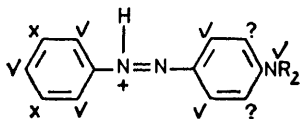

FIGURE 2 Applicability of Dewar's rules to azonium tautomers: $\sqrt{}$ signifies correct prediction of substituent effects by Dewar's rules, $\times$ signifies incorrect prediction of substituent effects by Dewar's rules, ? experimentally unknown substituent effect

The Applicability of Dewar's Rules to Neutral and Protonated 4-Aminoazobenzene Dyes.—The general trends reported in this paper for substituents in the 2-position of the neutral dyes (3) confirm the non-obeyance of Dewar's Rules [17] for groups in this position. Indeed,
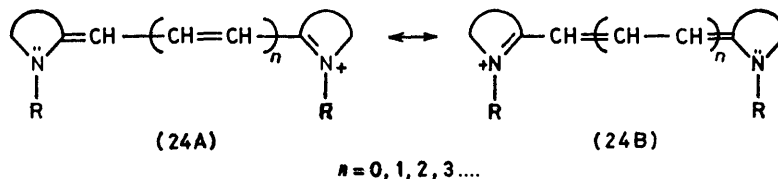
their general inapplicability to neutral 4-aminoazo-benzene dyes is evident when the experimentally determined effects of substituents are compared with predicted effects; the rules fail as often as they succeed! (Figure 1). Castelino and Hallas[6] were fortunate in that the 3- and 5-positions are ones for which the rules predict correctly the effect of substituents.

For the azonium tautomers (8), the effect of substituents on $\lambda_{max.}$ is opposite to that for the neutral dyes. As shown in Figure 2, Dewar's Rules are more applicable than in the case of the neutral dyes, with six successes, two failures, and two unknowns. However, for both the neutral and protonated dyes, the ' successes ' are limited

in that only the direction of the shift is predicted correctly: the magnitude is incorrectly predicted.

Dewar's Rules are derived from the application of PMO theory to odd alternant hydrocarbon (AH) anions; [17] for 4-aminoazobenzene dyes, the relevant odd AH ion is (23). Theory suggests that there should be no

(23)
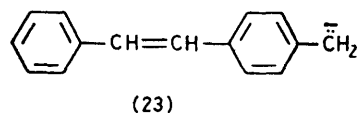
significant difference in bond order for these anions, *i.e.* the bond order tends to 1.6—1.7, rather than alternate single and double bonds. This condition holds in basic dyes and Dewar's Rules are, therefore, particularly applicable to these compounds. In symmetrical cyanine dyes, for example, the ground state is a resonance hybrid of the two equivalent canonical forms, (24A) and (24B); consequently, the bond order is 1.5.

In neutral 4-aminoazobenzene dyes, acceptable canonical forms of the uncharged structure (3) are charge-separated structures such as (4). The latter are of relatively high energy and contribute mainly to the excited state. The ground state of 4-aminoazobenzene dyes therefore approximates to (3), in which the bond order of the azo-group tends to 2 and that of the aryl-nitrogen bonds to 1. It is this lack of uniform bond order which is responsible for the failure of Dewar's Rules in the neutral dyes.

The azonium tautomers, because of the delocalised positive charge, resemble the basic dyes more closely. No charge separation occurs on going from the ground state to the excited state, only a redistribution of the positive charge. Bond uniformity is, therefore, greater than for the neutral dyes, so that Dewar's Rules become more applicable.

Valence Bond/resonance theory succeeds where

(24A) (24B)

$n = 0, 1, 2, 3....$

Dewar's Rules fail. For the neutral dyes, electronic excitation results in a migration of electron density from the amino-group and ring C, to the azo-group and ring D (1). An electron-donating substituent in any position of ring C, or an electron-withdrawing substituent in any position of ring D, stabilises the excited state relative to the ground state. This reduces the energy difference between the two states, causing a bathochromic shift of $\lambda_{max.}$. The converse is true if ring C contains electron-withdrawing substituents and ring D electron-donating substituents. Consequently, a hypsochromic shift of $\lambda_{max.}$ is observed.

Particularly pronounced shifts are observed for sub-

stituents at the amino-nitrogen atom;[2] presumably, this is the most electron-deficient centre. Because the nitrogen atom cannot accommodate more than eight valence electrons, only the inductive effects of the substituents operate.

or secondary anilino-coupling components. Spectroscopic data on such dyes are not available. However, steric effects were obviated in the azo-dyes (2) derived from julolidine, but the alkyl groups in the starred 3 and 5 positions of the azonium tautomer only produced a

(25A)   (25B)
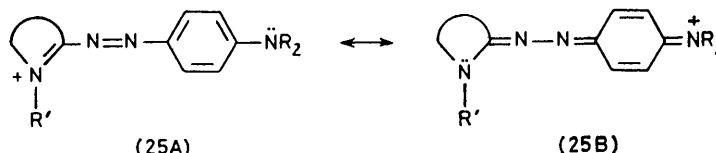
Substituent effects in ring D of the azonium tautomer (8) indicate that the quinonoid form (8B) makes the major contribution to the ground state! Structure (8A), which has two aromatic rings, is believed to pre-

bathochromic shift of 3 nm. Shifts of this magnitude are inconclusive and a detailed study of the effects of a range of electron-donating and electron-withdrawing substituents in the 3-position is required.
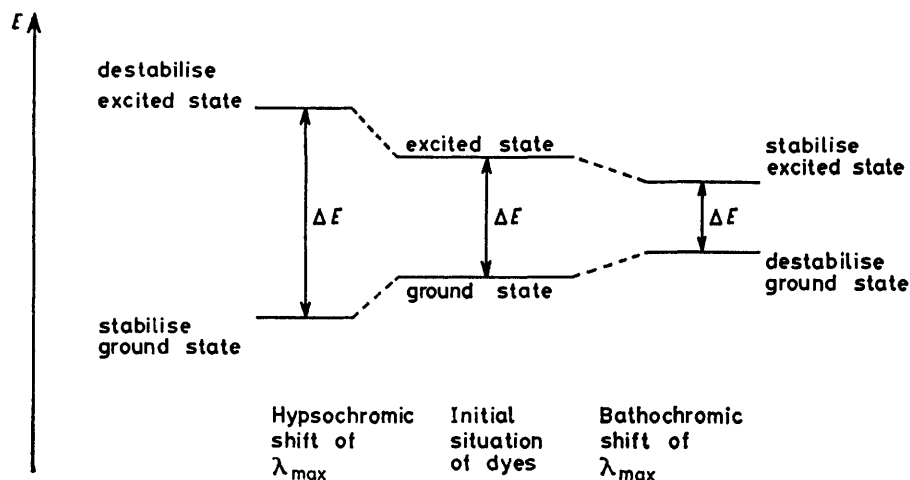

FIGURE 3   Effect of substituents on the energy levels of azonium and diazahemicyanine dyes

dominate in the excited state. A similar situation is encountered for diazahemicyanine dyes (25), where (25B) is the important limiting structure in the ground state.[8]

In the azonium tautomer, electronic excitation results in a migration of electron density from ring D to ring C (8). Electron-donating groups in any position of ring D stabilise the excited state and destabilise the ground state, causing a bathochromic shift of λ_{max}: electron-withdrawing groups have the reverse effect. In ring C, electron-donating groups stabilise the ground state and destabilise the excited state: a hypsochromic shift results. Again, electron-withdrawing groups cause the opposite effect. Figure 3 summarises schematically the effect of substituents on the energy levels of the ground and first excited state.

The above explanation assumes that electron-donating substituents in the starred 3 and 5 positions of the azonium tautomer produce a hypsochromic shift of λ_{max} and electron-withdrawing substituents a bathochromic shift, in contradiction of Dewar's Rules. Since only the electronic effects are being considered, dyes are required in which the substantial steric interaction between the 4-dialkylamino-group and a 3-substituent [7,27] is minimised; for example, dyes derived from primary

EXPERIMENTAL

Preparation of Coupling Components.—The majority of the coupling components were prepared by diethylation of the *meta*-substituted aniline with diethyl sulphate in water in the presence of an acid binding agent, usually sodium hydrogen carbonate. For the less basic amines such as *m*-fluoroaniline, *m*-nitroaniline, and *m*-aminoacetophenone, more forcing conditions were used, whereby the amine was dissolved in twice its volume of triethylamine at ambient temperature and a volume of diethyl sulphate, equal to that of triethylamine, added in one portion. Slight warming was applied to initiate a vigorous exothermic reaction, the temperature rising to *ca.* 120 °C. If necessary, the process was repeated in order to obtain complete diethylation. Typical examples of each method are given.

3-(NN-*Diethylamino*)*acetanilide.*   3-Aminoacetanilide (15 g) was stirred in water (75 ml) and sodium hydrogencarbonate (20.2 g). The temperature was raised to 50 °C and diethyl sulphate (37 g) was added dropwise during ¼ h. After stirring for a further 2 h at this temperature, the reaction was complete.* Water (150 ml) was added and the

* Determined by coupling a small sample of the reaction mixture with diazo-*p*-nitroaniline in aqueous acetone, spotting onto a silica gel t.l.c. plate and eluting with chlorobenzene–acetone–acetic acid (85 : 10 : 5). A single spot, bluer than the original starting material and of higher R_F value, indicated complete reaction.

mixture stirred and cooled to 0—5 °C. Scratching with a glass rod induced crystallisation and the resulting off-white solid was filtered off, washed with ice–water, and dried at 40 °C. A yield of 16.5 g was obtained.

3-(NN-Diethylamino)acetophenone. 3-Aminoacetophenone (2.7 g) and diethyl sulphate (6 ml) were placed in a boiling tube containing a thermometer. Triethylamine (6 ml) was added, and the reaction mixture gently stirred and allowed to exotherm to *ca.* 120 °C. The reaction was shown to be incomplete by the t.l.c. technique previously described. Therefore, the viscous liquid was poured into water (100 ml) and basified to Brilliant Yellow paper with

which were subsequently recrystallised to constant melting point, usually from ethanol or butanol. The elemental analysis results, recrystallisation solvents and melting points are recorded in Table 9.

2-Iodo-NN-diethylamino-4'-nitroazobenzene. 4-Nitroaniline (6.9 g) was dissolved in water (30 ml) and 10M-hydrochloric acid (15 ml) by heating to 70 °C; the hot solution was poured onto a mixture of ice–water (250 g). A solution of 2M-sodium nitrite (26 ml) was added to the resultant fine slurry and the reaction mixture stirred for ½ h at 0—5 °C to effect diazotisation. Sulphamic acid was then added to destroy the excess of nitrous acid and the

TABLE 9

Element analysis data, melting points, and recrystallisation solvents for dyes of formula (3)

X	Recryst. solvent	Required (%)				Found (%)				M.p. (°C)
		C	H	N	Other	C	H	N	Other	
F	Ethanol	60.7	5.4	17.7	6.0 (F)	61.0	5.5	17.9	5.7 (F)	145
NO₂	Light petroleum (b.p. 100—120 °C)	56.0	5.0	20.4		56.1	4.8	20.1		170—171
CN	Butanol	63.2	5.3	21.7		63.2	4.9	21.5		179
SO₂NMe₂	Butanol	53.3	5.7	17.3	7.9 (S)	52.9	5.6	17.0	7.6 (S)	183—185
SO₂Me	Methanol	52.7	5.4	15.4	8.8 (S)	53.7	5.1	14.3	8.9 (S)	213
Cl	Ethanol	57.7	5.1	16.8	10.7 (Cl)	57.4	4.8	17.2	11.7 (Cl)	140—142
Br	Ethanol	50.9	4.5	14.8	21.2 (Br)	50.7	4.4	14.8	21.4 (Br)	174
I	Ethanol and butanol	45.1	3.9	13.4	30.3 (I)	44.2	3.2	12.8	31.2 (I)	153—154
CO₂Et	Ethanol	61.6	6.0	15.1		61.8	5.8	15.1		111—112
SO₂NH₂	Dioxan	50.9	5.0	18.6	8.5 (S)	50.8	4.8	18.3	9.3 (S)	244—246
Ac	Ethanol	63.5	5.9	16.5		63.6	6.2	16.6		152—154
CO₂H	Ethanol	61.4	5.4	16.9		60.4	5.2	16.4		181—183
SO₂NHMe	Ethanol	52.2	5.4	17.9	8.2(S)	53.4	5.4	18.3	9.0(S)	197
O:P(OEt)₂	Ethanol	55.3	6.2	12.9	7.1 (P)	54.2	6.4	12.5	6.4 (P)	113
H	Ethanol	64.4	6.0	18.8		64.4	5.9	18.7		141—143
OH	Butanol	61.2	5.7	17.8		61.1	5.8	17.9		118—120
EtNAc	Butanol	62.7	6.5	18.3		62.6	6.7	18.3		180—183
Me	Ethanol	65.4	6.4	18.0		65.4	6.6	18.0		142—144
NHSO₂Me	Butanol	52.2	5.4	17.9	8.2 (S)	51.7	5.1	17.8	8.3 (S)	207—208
OMe	Ethanol	62.2	6.1	17.1		62.2	6.0	17.1		138—140
NHAc	Butanol	60.9	5.9	19.7		61.0	5.8	19.8		196—197
SMe	Butanol	59.3	5.8	16.3	9.3 (S)	59.8	6.0	16.3	10.3 (S)	160—163
NH₂	Butanol	61.3	6.1	22.4		61.1	6.1	22.2		188—189
NHCONH₂	Butanol	57.3	5.6	23.6		57.1	5.6	23.4		205—208
NEt₂		65.0	7.3	18.9		64.4	7.3	18.3		114

ammonia liquor. The mass was extracted with chloroform and the chloroform extracts dried (MgSO₄). After removal of the latter by filtration, the chloroform was evaporated off to leave a brown oil. The process was repeated and the reaction mass set aside for 2 days at ambient temperature. T.l.c. showed the reaction to be complete, and therefore the mass was worked up as described previously. A yield of 3.5 g was obtained.

Preparation of Dyestuffs.—All the dyes of formula (3), except for X = CN and O:P(OEt)₂, were prepared by diazotisation of *p*-nitroaniline followed by coupling to the appropriately *meta*-substituted *NN*-diethylaniline in aqueous hydrochloric acid solution buffered with sodium acetate. The dyes [3; X = CN and O:P(OEt)₂] were synthesised by the copper(I)-catalysed substitution of the preformed iodo-dye (3; X = I). The resulting azo-compounds were generally precipitated as crystalline solids

diazo-solution was filtered when cold.

The filtrate was added to a stirred solution of 3-iodo-*NN*-diethylaniline (13.8 g) in water (25 ml) and 10M-hydrochloric acid (6 ml) at 0—5 °C. After stirring for ¼ h, sufficient sodium acetate was added to remove the acidity to Congo Red paper. Acetone (200 ml) was added and the mixture stirred at 0—5 °C for 3 h and then for a further 18 h at ambient temperature. The resulting crystals were filtered off and the wet cake recrystallised from 95% ethanol (1.5 l) with the incorporation of a carbon screening stage. A yield of 7 g was obtained. After two further recrystallisations, 2.2 g of product were obtained which melted at 152 °C.

2-Cyano-4-NN-diethylamino-4'-nitroazobenzene. Cuprous cyanide (0.165 g) was dissolved in dimethylformamide (15 ml) at ambient temperature with stirring. 2-Iodo-4-*NN*-diethylamino-4'-nitroazobenzene (0.3 g) was added

and the solution stirred for 2 h at ambient temperature after which time the reaction was complete.* The solution was poured into cold water (200 ml) and the orange precipitate filtered off and dried to yield 0.35 g of product.

The product recrystallised from butanol as red needles (0.18 g) which melted at 179 °C.

Determination of the Electronic Spectra.—The u.v. and visible electronic absorption spectra were determined on a Unicam SP 800 recording spectrophotometer, in 2-mm and 5-mm cells for 10^{-4}M-solutions, and 20-mm cells for 10^{-5}M-solutions.

I.r. Spectra.—These were determined on a Perkin-Elmer 225 spectrophotometer calibrated with a polystyrene film. Spectra were obtained from the samples mulled in Nujol and also from 0.1% solutions in carbon tetrachloride using 1-cm cells with rock-salt plates.

In the solid state, the spectra of both the dyes (3; X = OH and CO_2H) contained broad bands in the region around 3 000 cm^{-1} normally attributed to hydrogen-bonding. In solution, the spectra contained the same broad bands, indicating that hydrogen-bonding was still occurring: this must be intramolecular bonding. There was no evidence of bands due to free hydroxy in the solution spectra. The carbonyl band of the carboxylic acid group moved from 1 735 cm^{-1} in the solid state to 1 745 cm^{-1} in solution, the latter corresponding to that of an intramolecularly bonded carboxylic acid forming a ring.

In the NH region, the sulphonamide dye (3; X = $NHSO_2Me$) gave bands at 3 320 cm^{-1} (solid) and 3 330 cm^{-1} (solution). The amide dye (3; X = NHAc) gave bands at 3 310 cm^{-1} (solid) and 3 390 cm^{-1} (solution). The band positions of the samples in solution are lower than expected for free NH, which indicates that an internal hydrogen-bond is being formed. In the case of the amide dye, the carbonyl band positions at 1 660 cm^{-1} (solid) and 1 700 cm^{-1} (solution) are as expected for bonded and free secondary amides.

The bands in the NH region of the dye (3; X = $NHCONH_2$) occurred at 3 400, 3 310, 3 370, and 3 200 cm^{-1} in very weak ($\ll 0.1$%) solution. The solution spectra were measured using cells with a 3-cm path length. In the carbonyl region, the spectra showed bands at 1 660 and 1 550 cm^{-1}, typical of urea in the solid state. In solution, three bands appeared at 1 715, 1 685, and 1 660 cm^{-1}. A

* Determined by t.l.c. as described previously but using as eluant, chlorobenzene–cyclohexane–ethanol–acetic acid (84 : 10 : 6 : 3).

spectrum of phenyl urea showed only a band at 1 705 cm^{-1} in solution. As the sample solution was very weak, the extra bands at 1 685 and 1 660 cm^{-1} indicate that intramolecular hydrogen bonding is occurring.

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